AN ABSORPTIOMETRIC METHOD FOR THE ESTIMATION OF ATMOSPHERE BENZENE

(IN THE PRESENCE OF XYLENE AND TOLUENE)

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The method for the detection of benzene in the atmosphere, described by Pfeiffer (1904) and Chavassieu and Morel (1906) and subsequently modified by Elliott and Dalton (1919), consisted of absorbing a sample of the air in a nitration mixture of sulphuric and nitric acids. This mixture was then neutralized and extracted with ether, and after evaporation of the ether meta-dinitro-benzene crystals were identified. For the quantitative estimation a number of methods have been suggested, most of which depend upon the formation of meta-dinitro-benzene, after absorption in a nitration mixture. Of methods based on other principles two are important: the first described by the Department for Scientific and Industrial Research (1939), and the second by Cook and Ficklen (1935). The first is the sulphuric formaldehyde method and is recommended for the control of benzene in factories. The atmosphere containing benzene is sucked through a solution of formaldehyde in sulphuric acid, when a brown colour develops. This colour is measured against standards. This method is an excellent sorting test, but is of doubtful value in work requiring accurate observation, since some colour is given by many hydrocarbons, including toluene, xylene and naphthalene, and almost any organic substance which chars in the presence of sulphuric acid will affect the result. This method will therefore give inaccurate results when estimations of atmosphere benzene are required in factories, where mixed solvents are in use, since benzene gives less colour than the other hydrocarbons. The second method is based on the red colour produced when ferrous sulphate solution and hydrogen peroxide are added to benzene. The air sample is drawn through a bubbler U-tube trap which is immersed in solid carbon dioxide. The benzene which condenses is distilled into a second trap after scrubbing with water. Ferrous sulphate and hydrogen peroxide solutions are then added and the red colour measured optically. The method is claimed to be highly specific for benzene, but it suffers from the disadvantage of being relatively insensitive, since not more than 5 mg. of benzene are detectable. The products of the reaction probably include phenol, hydroquinone, catechol and the black oxidation product of variable composition when larger quantities of benzene are present.

Most techniques for benzene estimation involve some form of reaction after nitration. One method depends on the colour given when the products of nitration are heated with sugars (Pérronet, 1933). There is, however, some doubt as to the reproducibility of the colour, since Szécsényi-Nagy (1935) has suggested that only the ortho isomer of dinitro-benzene is involved in this reaction, despite the fact that the bulk of the products of nitration consists of meta-dinitro-benzene. The sensitivity is therefore much diminished. A second method, described by Jacobs (1941), consists of reducing the dinitro-compound with zinc dust to metaphenylene diamine. This is then diazotized with nitrous acid and coupled with α -naphthol to produce an intense brown colour. This method is very sensitive but not specific.

A titrimetric technique has been described by Smyth (1929). This consists of separating the meta-dinitro-benzene from the nitration acids by steam distillation and then reducing to the diamine with an excess of titanous chloride solution. It was then titrated with standard ferric alum. The method may be made almost specific for benzene, but it is not suitable for small quantities and is rather tedious to perform.

The most suitable of the dinitro-benzene methods are those which depend on the colour reaction with a ketone in alkaline solution. This technique has been elaborated by Schrenk, Pearce and Yant (1935, 1936) for the estimation of benzene in factory air. These authors absorb the benzene in a mixture of fuming nitric and sulphuric acids and extract the meta-dinitro-derivative with butanone. It is then rendered alkaline with caustic soda and a blue-red colour results which may be measured colorimetrically.

This technique is not specific for benzene, since toluene gives a similar colour, although to about 1/20th of the intensity, and xylene gives a green colour, also of low sensitivity. Colours are also given by mono-substituted benzene-derivatives and naphthalene.

Hence, when the concentration of benzene alone is required where other hydrocarbons may be present, Schrenk's method cannot be utilized. The technique, however, has been modified by Dolin (1943) to be more specific for benzene. When meta-dinitro-benzene is extracted with ether from

the nitration mixture and treated with butanone, alcohol and alkali, the colours due to xylene and toluene are destroyed on acidification, but that due to benzene is permanent. The modification has a number of disadvantages. It requires extraction from the nitration mixture with ether, with possibilities of loss during the manipulative and washing procedures. The subsequent estimation of the benzene is made on 1/25th of the amount of benzene absorbed from the air, thus reducing the sensitivity of the method. Lastly, the yellow colour given on nitration by toluene and xylene is not accurately allowed for during the colorimetric procedure.

Since the meta-dinitro-benzene butanone compound is stable in acid solution, whereas the nitro-derivatives of the other substances are destroyed, a method has been elaborated whereby the disadvantages of Dolin's technique are overcome.

The vapours are absorbed in a bead bubbler charged with nitration mixture. The contents of the bubbler are diluted with water and neutralized with caustic soda. The nitro-derivatives are extracted with butanone, and the yellow colour imparted to the butanone by the nitro-derivatives of toluol and xylol is measured in a Spekker photoelectric absorptiometer. The mixture is rendered alkaline and the colours allowed to develop. The solution is then made acid with acetic acid, when the bluish-green colour, due to the reaction of toluene and xylene with butanone and alkali is destroyed, but that due to benzene persists. A second photoelectric reading is then taken. The difference between the two readings represents the colour due to benzene. In this way the basic yellowish colour due to nitro-toluenes and nitro-xylenes which is persistent in the presence of acid or alkali may be allowed for.

Details of Method

1. Absorbing Solution.

A mixture of equal parts of concentrated sulphuric and fuming nitric acids is used. This mixture will quantitatively convert benzene in the cold to the meta-dinitro-derivative in 30 minutes, provided that the volume of the benzene is less than one-tenth that of the nitration mixture. In the absence of sulphuric acid the nitration of benzene is varied and incomplete, and there is also a tendency to form mono-nitro-benzene unless fuming nitric acid is used.

2. Sampling Procedure.

A bead bubbler is charged with 10 ml. of the nitration mixture. The atmosphere is aspirated through the solution at a rate of 1 litre per minute, since at this speed absorption of benzene from the air is quantitative. At 5 litres/minute or more there is a tendency to lose about 5 per cent. of the benzene, but this may be overcome if two bead bubblers are coupled in series. In the absorption train the bubbler is followed first by an absorption bottle containing 40 per cent. caustic soda to absorb nitric fumes aspirated from the acid mixture, and then by a flow-meter to indicate the rate of sampling. The apparatus is operated by an air injector of the Venturi type attached to a compressed air bottle. Where very low concentrations of benzene are present an absorber containing 2 ml. of mixture is used.

3. Colour Development.

After taking the sample an interval of 30 minutes should elapse to allow nitration to complete. The sample may, however, be left at this stage for an indefinite period without any deterioration.

Two ml. of the acid mixture from the bubbler are transferred to a 50 ml. Erlenmeyer flask, and diluted to 10 ml. with water. This is then neutralized with 40 per cent. caustic soda. Care should be taken to see that the solution is just alkaline to litmus, since the colour is impaired if the solution is left acid, and if it is too alkaline premature development of the colour occurs.

Ten ml. of pure butanone is then added and the mixture shaken over a period of 10 minutes. After separation of the two layers the butanone layer is removed to a test-tube to which is added 30 ml. of absolute alcohol. Extraction of benzene is complete by this procedure, although in the presence of xylene and toluene a partition of the yellow colour between the two layers occurs. If much toluene and xylene is present the butanone is coloured yellowish-brown, and this colour persists after alkalization and subsequent acidification. Consequently the optical density of this solution must be measured and allowance made accordingly. If coloured the butanone solution is transferred to the Spekker absorptiometer fitted with a green screen, and a reading taken (Reading I). If the solution is colourless at this stage, then this reading may be dispensed with.

The alcohol-butanone solution is then treated with 0.1 ml. of 40 per cent. caustic soda solution and mixed. In the presence of benzene a red colour develops fully within 5 minutes. A purple or green colour due to toluene and xylene respectively shows up if these substances are present, with varying shades of intensity according to the mixture. The amount of soda to be added is not critical, but the bulk of water in solution must be kept to a minimum in order to ensure solution in the alcohol-butanone mixture.

Five minutes is allowed for the alkaline colour to develop completely, although this usually occurs within two minutes of mixing with the soda; 0.1 ml. of glacial acetic acid is then added and the whole mixed. The alkaline colours due to xylene and toluene are completely destroyed, leaving a reddish colour due to dinitro-benzene and the residual yellow colour of the butanone extract. The destruction of the xylene and toluene colour is immediate, and so the final Spekker reading may be made forthwith. Again the measurement is made with the green screen fitted in the instrument. The difference between this reading and that of the butanone extraction solution represents colour due to the benzene. The acidified colour is stable, and so the reading may be deferred for some hours if necessary.

The result is referred to a calibration curve constructed by submitting standard solutions of benzene to the technique described; 50 mg. of benzene is weighed in a closed vessel and dissolved in 100 ml. of absolute alcohol; 1 ml. of this solution will contain 500 μ g. of benzene. From this solution 5 dilutions in absolute alcohol are made to contain 100, 200, 300, 400 and 500 μ g. of benzene per ml. By means of a specially calibrated pipette 0.1 ml. of each of these solutions is added to 2 ml. of the nitration mixture, allowed to stand for

TABLE 1

Concentration of Benzene	Spekker difference	Concentration of Hydrocarbon	Spekker difference
0 μ g.	0.00	0 μ g. Benzene plus 500 μ g. Toluene	0.00
10 μ g.	0.14	10 μ g. " " "	0.16
20 μ g.	0.29	20 μ g. " " "	0.31
30 μ g.	0.41	30 μ g. " " "	0.39
40 μ g.	0.54	40 μ g. " " "	0.52
50 μ g.	0.68	50 μ g. " " "	0.68

30 minutes and then treated to develop the colour as described above. The reading differences are plotted against concentration. This gives a calibration curve up to 50 μ g. of benzene, which is the sensitive range of the method. Thus sampling at 1 litre per minute 100 μ g. of benzene will be collected in about 30 minutes if the concentration of benzene in the atmosphere to be sampled is 1 part per million.

The technique described above will readily measure benzene in the presence of 20 times the concentration of xylene or toluene. If the concentration of these substances is much higher, then the yellowish-brown colour due to their nitration products is so large in comparison with the reddish hue due to benzene as to make difference readings questionable.

Table 1 shows the calibration curves for benzene alone, and in the presence of 500 μ g. to toluene. It will be seen that the two curves are for practical purposes identical.

TABLE 2
EFFECT OF VARYING AMOUNTS OF
XYLENE AND TOLUENE

Concentration (in μ g.)			Reading I	Reading II	Difference
Benzene	Toluene	Xylene			
20	—	—	0.01	0.31	0.30
20	50	—	0.03	0.32	0.29
20	500	—	0.19	0.49	0.30
20	—	500	0.06	0.36	0.30
20	—	1000	0.09	0.38	0.29
20	1000	—	0.35	0.63	0.28
20	500	500	0.26	0.56	0.30
50	—	—	0.01	0.69	0.68
50	50	—	0.03	0.72	0.69
50	500	—	0.19	0.87	0.68
50	1000	—	0.30	1.00	0.70
50	—	500	0.05	0.72	0.67
50	—	1000	0.08	0.78	0.70
50	500	500	0.31	1.01	0.70

Note. The brown colour due to xylene and toluene is not consistent since it varies with the rate of neutralization, temperature, etc., but is always the same before and after the colour development procedure.

Numerous experiments have been carried out with varying concentrations of xylene and toluene as shown in Tables 2 and 3, indicating that interference due to these substances is negligible.

TABLE 3
EFFECT OF TOLUENE AND XYLENE

Concentration	Reading I	Reading II	Difference
50 mg. toluene ..	0.03	0.03	nil
500 mg. " ..	0.19	0.19	nil
1000 mg. " ..	0.35	0.35	nil
500 mg. xylene ..	0.06	0.06	nil
1000 mg. " ..	0.08	0.08	nil

Summary

A method is described for the estimation of benzene in the atmosphere in the presence of high concentrations of xylene and toluene.

Details of the sampling technique are given and the conditions necessary for consistent findings have been investigated.

Figures are given in support of the efficiency of the method.

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